

# PATENT SPECIFICATION

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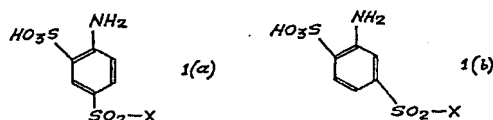
C2C 200 220 227 22Y 292 29Y 30Y 321 32Y 360 361 36Y 391  
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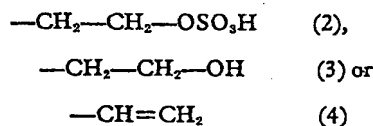
## (54) PROCESS FOR THE PRODUCTION OF 1-AMINOBENZENE-4- AND -5-β-SULPHATOETHYLSULPHONE-2-SULPHONIC ACID AND THEIR HYDROXYETHYLSULPHONE- AND VINYLSULPHONE DERIVATIVES

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 SCHAFT, a body corporate organised accord-  
 ing to the laws of the Federal Republic of  
 Germany, of 6230 Frankfurt/Main 80, Post-  
 fach 80 03 20, Federal Republic of Germany,  
 do hereby declare the invention for which we  
 pray that a patent may be granted to us,  
 and the method by which it is to be per-  
 formed, to be particularly described in and  
 by the following statement:—

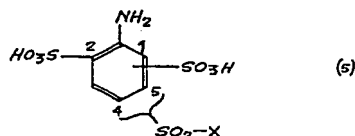
The present invention provides a process  
 for the production of compounds of the  
 general formulae 1(a) and/or 1(b)



wherein X represents a group



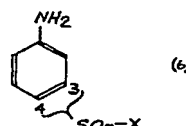
which comprises treating a corresponding  
 compound of the general formula (5)



wherein X has the above meanings in an  
 aqueous mineral acid having an acid con-  
 centration of 1 to 99% by weight, preferably  
 30 to 96% by weight, at a temperature of  
 from 80 to 140°C, preferably 100 to 130°C.  
 Mineral acids which may be used are hydro-  
 chloric acid, phosphoric acid and preferably  
 sulphuric acid. For splitting off the sulphonic

acid group, a compound of the general formula  
 (5) is dissolved in water, the solution is mixed  
 with mineral acid, for example hydrochloric  
 acid, phosphoric acid or sulphuric acid, and  
 heated under normal pressure or under in-  
 creased pressure to 80—140°C, in which  
 process an increase in the acid concentration  
 by distilling off water may simultaneously take  
 place. It is advantageous to proceed as fol-  
 lows:

a sulphonation batch obtained by sulphona-  
 tion in which a starting compound of the  
 formula (6)



wherein X represents a radical of the above  
 formulae (2), (3) or (4) has been preferably  
 reacted with a mixture of sulphuric acid and  
 sulphur trioxide or a mixture of sulphuric  
 acid and chlorosulphonic acid (the molar ratio  
 between the starting product of the formula  
 (6) and sulphur trioxide or chlorosulphonic  
 acid may be from 1:2.2 to 1:3) at a tem-  
 perature of from 90 to 150°C, preferably  
 from 100 to 130°C to yield either a pure  
 compound of the general formula (5) or a  
 mixture of a compound of formula (5) with a  
 quantitatively secondary portion of from 1  
 to 10% of a compound of the general formula  
 (1), is preferably mixed with water or with  
 an aqueous dilute mineral acid containing  
 from 30 to 99% of water preferably from 80  
 to 95%, and heated to a temperature of from  
 80—140°C, preferably 100 to 130°C, to  
 obtain a quantitative splitting to form a pure  
 compound of the general formulae (1).

The compounds of formulae (1) may be  
 isolated from the solutions of mineral acids  
 after neutralization with alkali metal or  
 alkaline earth metal hydroxides or carbonates  
 by salting out with alkali metal halides or by

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spray-drying. When using a large excess of acid, for example sulphuric acid which is used as described above in the sulphonation process of the preliminary stage, the mixture is advantageously neutralised to about 85% with calcium oxide or carbonate and finally with about 15% of sodium hydroxide, the calcium sulphate semi-hydrate precipitated is then separated above 65°C, and the desired compound of formula (1) is then isolated by spray-drying or salting out with sodium or potassium chloride.

When a mineral acid having a water content of more than 30% by weight is used, a compound of the general formulae (1) wherein X represents the group  $-\text{CH}_2-\text{CH}_2-\text{OH}$  (3) is principally obtained, which after isolation and drying may be converted by esterification with 95 to 100% sulphuric acid at 0–40°C, preferably 20 to 30°C, into a compound of formulae (1) wherein X represents the radical  $-\text{CH}_2-\text{CH}_2-\text{OSO}_3\text{H}$  (2). Compounds of formulae (1) wherein X represents the radical  $-\text{CH}=\text{CH}_2$  (4) may also be obtained from compounds of formulae (1) wherein X represents the formula  $-\text{CH}_2-\text{CH}_2-\text{OSO}_3\text{H}$  (2), by treatment with aqueous alkalis at 20 to 100°C, preferably at 40–70°C.

The preparation of compounds of the general formulae (1) from compounds of the general formula (5) is a new process and was not foreseeable. The reaction proceeds quantitatively and yields very pure end products so that the known compounds of the formulae (1) are obtained having regard to the state of the art in purer form and higher yield according to a process which may be carried out on an industrial scale.

Thus, for example 1 - aminobenzene - 4 -  $\beta$  - sulphatoethylsulphonic acid is obtained according to a process described in German Offenlegungsschrift No. 2,154,943 in yields of from 70 to 80% of theory by sulphonation of 1 - aminobenzene - 4 -  $\beta$  - sulphatoethylsulphone with nearly stoichiometrical amounts of  $\text{SO}_3$ ; the remaining 20 to 30% is to a large extent an unsulphonated starting product. According to the novel process of the invention the desired compound is obtained after sulphonation with an excess of  $\text{SO}_3$  and subsequent resplitting, in pure form with a yield of 95 to 98% of theory.

The 1 - aminobenzene - 5 -  $\beta$  - sulphatoethylsulphone - 2 - sulphonic acid formed during desulphonation of 1 - aminobenzene - 5 -  $\beta$  - sulphatoethylsulphone - 2,4 - disulphonic acid which may be obtained according to the sulphonation process of German Offenlegungsschrift No. 2,352,059, was found to be structurally identical, after treatment with alkalis in order to convert it into the corresponding vinyl sulphone compound, with the compounds obtained from 1 - chloro - 2 - nitrobenzene - 4 - sulphochloride by reduction

to the sulphonic acid and reaction with ethylene oxide to form 1 - chloro - 2 - nitrobenzene - 4 -  $\beta$  - hydroxy - ethylsulphone, substitution of the chlorine by means of an alkali sulphite to yield the 1 - nitrobenzene - 5 -  $\beta$  - oxyethylsulphone - 2 - sulphonic acid, followed by reduction to the corresponding amino compound, esterification with 100% sulphuric acid to form 1 - amino - 5 -  $\beta$  - sulphatoethylsulphone - 2 - sulphonic acid and conversion into the vinyl compound by treatment with alkalis. This process can only be carried out on a technical scale by using important protective measures since 1 - chloro - 2 - nitrobenzene, - 4 - sulphochloride and 1 - chloro - 2 - nitrobenzene - 4 -  $\beta$  - hydroxyethyl sulphone cause injuries to the skin and allergies. According to the novel process of the invention, however, the desired compounds can be produced without any risk.

The compounds of the general formulae (1) are valuable starting products for the manufacture of dyestuffs as described in German Offenlegungsschriften Nos. 2,154,942; 2,161,760 and 2,222,032.

The following Examples illustrate the invention. Parts and percentages are by weight unless otherwise stated.

#### EXAMPLE 1:

343 Parts of 1 - aminobenzene - 5 - vinylsulphone - 2,4 - disulphonic acid were dissolved in 2000 parts of water. After dropwise addition of 250 parts of 100% sulphuric acid while maintaining the temperature of the mixture at about 20°C by external cooling, the mixture was heated for 4 hours at 110–120°C and 1000 parts of water distilled off. After cooling to room temperature the precipitated 1 - amino - benzene - 5 - vinylsulphone - 2 - sulphonic acid was suction-filtered. The yield was 95% of theory.

#### EXAMPLE 2:

343 Parts of 1 - aminobenzene - 5 - vinylsulphone - 2,4 - disulphonic acid was stirred into 3000 parts of 31% hydrochloric acid. After refluxing for 2 hours the 1 - aminobenzene - 5 - vinylsulphone - 2 - sulphonic acid was obtained after cooling to room temperature. The yield was 99% of theory.

#### EXAMPLE 3:

343 Parts of 1 - aminobenzene - 5 - vinylsulphone - 2,4 - disulphonic acid was stirred into 800 parts of water, mixed with 250 parts of ortho - phosphoric acid and heated under reflux for 4 hours. The 1 - aminobenzene - 5 - vinylsulphone - 2 - sulphonic acid was obtained in a quantitative yield and could be further processed directly without purifying or intermediate isolation, for example by diazotisation and coupling to form an azo dyestuff.

## EXAMPLE 4:

50 Parts of 1 - aminobenzene - 5 -  $\beta$  - sulphatoethylsulphone - 2,4 - disulphonic acid were heated in 150 parts of 60% sulphuric acid for 4 hours at 100°C. After this process  $\beta$  - sulphatoethylsulphone group had been saponified to form the  $\beta$  - hydroxyethylsulphone group, and the sulphonic acid group in 4-position split off. The yield of 1 - aminobenzene - 5 -  $\beta$  - hydroxyethylsulphone - 2 - sulphonic acid was quantitative.

## EXAMPLE 5:

281 Parts of 1 - aminobenzene - 3 -  $\beta$  - sulphatoethylsulphone were introduced portionwise at 15—20°C while cooling and stirring and with exclusion of air humidity, into 843 parts of 100% sulphuric acid. After one hour 350 parts of oleum containing 65% by weight of SO<sub>3</sub> were slowly added dropwise, the temperature being maintained at 15—20°C by external cooling. The mixture was then heated for 12 hours at 130°C until the sulphonation to form 1 - aminobenzene - 5 -  $\beta$  - sulphatoethylsulphone - 2,4 - disulphonic acid was finished, slowly mixed at the same temperature with 265 parts of 50% aqueous sulphuric acid and heated for another 12 hours at 130°C. After cooling to 25°C the whole was poured on to ice. 780 Parts of calcium oxide were added, and the pH value adjusted to 6.0 with calcined sodium carbonate. The whole was then heated to 70°C. After filtering from the calcium sulphate semi-hydrate the 1 - aminobenzene - 5 -  $\beta$  - sulphatoethylsulphone - 2 - sulphonic acid was isolated as the sodium salt by evaporation to dryness. The yield was 85% of theory.

## EXAMPLE 6:

5 Parts of 1 - aminobenzene - 5 -  $\beta$  - hydroxyethylsulphone - 2,4 - disulphonic acid were heated in 15 parts of 15% sulphuric acid for 8 hours at 80°C. The 1 - aminobenzene - 5 -  $\beta$  - hydroxyethylsulphone - 2 - sulphonic acid was obtained in quantitative yield after neutralization of the solution with an aqueous sodium hydroxide solution and evaporation to dryness.

## EXAMPLE 7:

281 Parts of 1 - aminobenzene - 4 -  $\beta$  - sulphatoethylsulphone were introduced into 554 parts of 100% sulphuric acid, whereby the temperature increased to 35°C. Then 350 parts of 65% oleum were added dropwise and the reaction mixture heated for 5 hours at 100°C while stirring and with exclusion of air humidity until the starting product could no longer be detected. 88 Parts of 50% sulphuric acid were added to the mixture and heating continued for another 5 hours at 100°C for splitting off the second sulphonic acid of the starting product. After stirring and cooling to 25°C the mixture was poured onto ice while

stirring, buffered with 950 parts of calcium carbonate, adjusted to pH 6 with sodium carbonate and, after heating to 70°C, separated from the precipitated calcium sulphate semi-hydrate. The 1 - aminobenzene - 4 -  $\beta$  - sulphatoethylsulphone - 2 - sulphonic acid was isolated as the sodium salt by evaporation. The yield was 96% of theory.

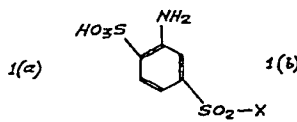
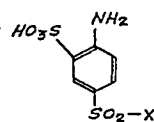
This compound thus prepared could be further processed directly in the solution, without evaporation or spray-drying for example by diazotisation and coupling.

## EXAMPLE 8:

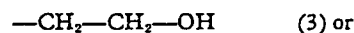
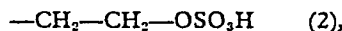
281 Parts of 1 - aminobenzene - 4 -  $\beta$  - sulphatoethylsulphone were introduced into 554 parts of 100% sulphuric acid and stirred. After addition of 332 parts of chlorosulphonic acid the mixture was heated with exclusion of humidity for 3 hours at 140°C until the starting product had completely disappeared. The mixture was subsequently stirred while cooling to 25°C, introduced while stirring into ice and then neutralized successively with 950 parts of calcium carbonate and 160 parts of sodium carbonate. After heating to 70°C the mixture was filtered from calcium sulphate semi-hydrate and the solution evaporated to dryness. The mixture consisting of about 10% of 1 - aminobenzene - 4 -  $\beta$  - sulphatoethylsulphone - 2 - sulphonic acid sodium salt and about 90% of 1 - aminobenzene - 4 -  $\beta$  - sulphatoethylsulphone disulphonic acid di-sodium salt was dissolved in 2000 parts of water, mixed with 250 parts of 100% sulphuric acid and heated at 80°C for 10 hours until the second sulphonic acid group in the intermediate product was completely split off to form the monosulphonic acid. After neutralizing the excess acid with calcined sodium carbonate, the 1 - aminobenzene - 4 - hydroxyethylsulphone - 2 - sulphonic acid was obtained with about 98% purity by evaporation to dryness it could be converted into the corresponding 1 - amino - benzene - 4 - sulphatoethylsulphone - 2 - sulphonic acid by esterification with 100% sulphuric acid at temperatures of about 20°C.

## WHAT WE CLAIM IS:—

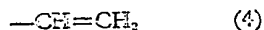
1. A process for the production of a compound of the general formulae 1(a) and/or 1(b)



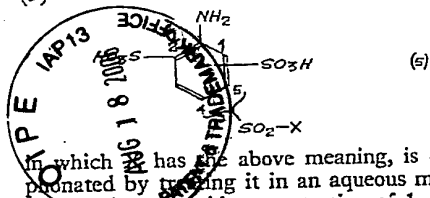
wherein X represents a group



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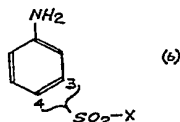
wherein a compound of the general formula (5)



5 in which has the above meaning, is desulphonated by treating it in an aqueous mineral acid having an acid concentration of 1—99% by weight at a temperature of from 80 to 140°C under atmospheric pressure or under increased pressure.

10 2. A process as claimed in claim 1, wherein the aqueous mineral acid used contains 30 to 96% by weight of sulphuric acid.

15 3. A modification of the process as claimed in claim 1 or 2, which comprises sulphonating a compound of formula (6)



20 wherein X represents the groups as defined in claim 1, at a temperature of from 90 to 150°C, subsequently mixing the reaction solution with water or with a mineral acid diluted with water, and heating at a temperature of from 80 to 140°C.

4. A process as claimed in claim 3 wherein the sulphonation of a compound of formula (6) is carried out with a mixture of sulphuric acid and sulphur trioxide or a mixture of sulphuric acid and chlorosulphonic acid.

5. A process as claimed in claim 3 or 4 wherein the sulphonation product is diluted with a mineral acid containing from 30 to 99% of water.

6. A process as claimed in any one of claims 3 to 5 wherein the mineral acid used is sulphuric acid.

7. A process as claimed in any one of claims 1 to 6 carried out substantially described herein or in any one of the Examples.

8. A process wherein a compound produced according to claim 1 is used for the synthesis of azo dyestuffs.

9. Azo dyestuffs which have been produced with any one of the compounds prepared as claimed in any one of claims 1 to 6.

10. The compounds which have been produced as claimed in any one of claims 1 to 6.

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Reference has been directed in pursuance of section 9, subsection (1) of the Patents Act 1949, to patent No. 1,380,234.